1953

The effect of cross-linkage on internal diffusion in Dowex-50 ion exchange resin

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THE EFFECT OF CROSS-LINKAGE ON INTERNAL DIFFUSION IN DOWEX-50 ION EXCHANGE RESIN

A Thesis

Presented to

The Faculty of the Department of Chemistry

College of Pacific

In Partial Fulfillment

Of the Requirements for the Degree

Master of Arts

by

John Paul Peterson Jr.

June 1953

ACKNOWLEDGMENT

The author wishes to express his appreciation to the faculty of the Department of Chemistry, especially to Dr. Don C. DeVault for his invaluable help on the theoretical parts of the problem, and to the Dow Chemical Company for the experimental resins used.

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FOREWORD

As far back as the time of Aristotle sand filters were used to purify water. However it was not until the time of Thompson and Way (1848), two English agricultural chemists, that the idea of actual exchange of ions was proposed. Ion exchange has been investigated extensively, resulting in applications to softening of water, purification of sugar, separation of compounds, recovery of metals, many pharmaceutical separations and many others.

It has been proposed that the internal diffusion should be related to the internal structure of the ion exchange resin. The object of this research was to measure the internal diffusion and relate it to the cross-linkage of the resin. It was suggested by Dr. Theodore Vermeulen of the Chemical Engineering Department, University of California. He proposed that the external diffusion could be eliminated by having a high rate of flow in the column. By measuring the width of the zone formed, the rate constant could be found. The rate constant is proportional to the diffusion rate.

REVIEW OF LITERATURE

HISTORICAL BEGINNING OF ION EXCHANGE AND RESINS

Fuch, in 1833, reported that certain clays when treated with lime gave up sodium and potassium ions. However the credit for the discovery of ion exchange is generally given to H. S. Thompson and J. T. Way, two English agricultural chemists. In 1848, they reported that on treating a soil with either ammonium sulfate or carbonate most of the ammonia was adsorbed and lime was released. J. T. Way continued the investigation until 1854 when he presented his conclusions to the Royal Agricultural Society of London. His conclusion as reported by Kunin and Myers, "Ion Exchange Resins", page 2, are:

> (1) the exchange of calcium and ammonium ions in soils noted by Thompson was verified. (2) Exchange of ions in soils involved the exchange of equivalent quantities. (3) Certain ions were more readily exchanged than others. (4) The extent of exchange increased with concentration, reaching a leveling off value. (5) The temperature coefficient for the rate of exchange was lower than that of a true chemical reaction. (6) The aluminum silicates present in soils were responsible for the exchange. (7) Heat treatment destroyed the exchange. (8) Exchange materials could be synthesized from soluble silicates and alum. (9) Exchange of ions differed from true physical adsorption.

Way's work was rather extensively continued by Boedeker, Peters, Wolff, Frank, Sestini, Eichorn and others (Kunin and Myers 1950).

In 1876, the next significant contribution was made by E. Lemberg, who found that the mineral, leucite,

could be changed to analcite by treating it with a solution of sodium chloride. This was reversed by treating the analcite with a solution of leucite. This experiment showed the reversibility of the ion exchange process.

Even though the work of Way, Thompson, Lemberg, and others has advanced the knowledge of ion exchange, it was not until 1906 that it was applied in industry. In 1906, Robert Gans, a German professor, first tried to use synthetic aluminum silicates for water softening and the treatment of sugar solutions. It was then that ion exchange phenomena were first really seriously explored. It is interesting to note that his initial idea was to obtain the gold from sea water but his investigations resulted in a process for softening of water. The work continued, centering around the study of clays, soils, and other silicates. It was not until considerable work had been done on the relationship of structure of the silicate to it's exchanging properties the principle of ion exchange was understood.

It was in this period of study and trial applications to industry that the limitations of siliceous exchangers were recognized. The discovery by B. A. Adams and E. L. Holmes in 1935 that certain synthetic resins exchanged ions was a welcome avenue of exploration. Adams

and Holmes showed that certain sulfonic acid resins would serve as stable high capacity cation exchangers and that their stability at various pH's made these resins valuable in many new processes. These workers were the first to synthesize a resin which would exchange anions. These anion resins were of a polyamine-type. Holmes' patents were obtained by Rohm and Haas in the United States and I. G. Farben Industries in Europe. Four chemical companies, Rohm and Haas, Chemical Process Company, Dow Chemical Company, and American Cyanamid, in the United States started to manufacture exchange resins.

The next advance came when G. F. D'Alelio of General Electric found that styrene made an excellent resin base. The most recent advance was by Walter Juda of Massachusetts Institute of Technology who has developed an ion exchange membrane.

Some of the uses of ion exchange materials are the separation of fission products (Fortune 1951), treatment of peptic ulcers (Fortune 1951), to remove calcium from blood to prevent coagulation (Fortune 1951), and separation of amino acids (Winters and Kunin 1949).

THEORIES PRESENTED TO EXPLAIN ION EXCHANGE

Parallel to the work being done on synthesis or exploration of ion exchanging materials, there were developing various theories on the exchange itself. They fall into three general cases: (1) the crystal lattice structure theory, (2) the double-layer theory, and (3) the Donnan theory.

Crystal lattice structure theory. In the crystal the constituents are considered ions, therefore the crystal is completely dissociated. The ions at the surface are not held as tightly as the internal ions. In a polar medium such as water, the interionic attraction is of such a magnitude that the net attractive force is small enough to permit exchange. The six things that the exchange depends upon are: (1) the nature of the forces binding the ion to the crystal, (2) the concentration of the exchanging ion, (3) the charge of the exchanging ion, (4) the sizes of the two ions, (5) the accessibility of lattice ions, and (6) the solubility effects (Kunin and Myers 1950).

Double-layer theory. The double layer theory, proposed by Helmholtz (1879) as an explanation of the electrokinetic properties of colloids, has been considered as an explanation of ion exchange. The Helmholtz model consists of an inner layer of fixed charge and an outer layer of mobile charge. The ions in the outer layer are diffused

into the external medium. We can consider the concentration to vary continuously to the inner layer thus creating a film of varying concentration. The concentration of the layer is dependent upon the concentration and the pH of the solution.

Donnan theory. The Donnan theory is essentially a special case of the Donnan membrane theory (Donnan 1924). The Donnan theory pertains to the unequal distribution of ions on two sides of a membrane, one side contains an electrolyte, one of whose ions is not able to diffuse through the membrane. In the case of ion exchange resins, the resin would be the nondiffusable ion. Although no membrane is encountered in ion exchange equilibria, the interface between the solid and liquid phases may be considered as a membrane. The Donnan theory does not conflict with crystal lattice theory but merely offers a quantitative relationship governing the exchange of ions. In many simple ionic solids all ions may be capable of diffusion, and hence the Donnan theory cannot be applied. It has been shown that the Donnan theory is not quantitatively followed in dilute solutions (Bauman and Eichhorn 1947).

All of the ion exchange theories are quite similar in that the exchange of ions must satisfy the law of

electoneutrality. The only differences in the various theories then are the position and the origin of the exchange site. The laws governing the exchange of ions in these heterogenous systems are therefore quite analogous to those governing the solutions of electrolytes (Kunin and Myers 1950).

One of the other theoretical approaches which has been studied extensively is the relationship between the extent of exchange and concentration. The various attempts fall into two types, one assuming simple adsorption and the other applying the law of mass action.

Adsorption. Soon after the initial experiments of Way's on ion exchange Boedeker suggested the equation

$$X = ka^n$$

where X is the quantity adsorbed, a is the initial quantity of electrolyte added, and k, n are constants. G. Wiegner (1912) applied the Freundlich isotherm giving the relationship

$$\frac{x}{m} = kc^{1/p}$$

where c is the equilibrium concentration, $\frac{x}{m}$ is the amount adsorbed per gram of adsorbant, and k, p are constants. Later G. Wiegner and Jenny (1927) realized they did not indicate a finite capacity therefore the equation was modified to

$$\frac{x}{m} = k\left(\frac{c}{a - c}\right)^{1/p}$$

where a is the initial concentration and the other symbols are the same. Different equations of this type have been used extensively but L. Weisz (1932) considered none of them to be satisfactory over a large enough range of conditions.

Recently Boyd, Schubert and Adamson (1948) used an equation employing the Langmuir type isotherm, for the adsorption of ions, A, from an electrolyte solution.

$$\left[\frac{X}{m}\right]_{A^+} = \frac{kb_1 \quad C_{A^+}}{1 + b_1 C_{A^+} + b_2 C_{B^+}}$$

where $(X/m)_{A^+}$ is the amount of A ion adsorbed per unit weight of exchanger, C_{A^+} and C_{B^+} are the activities of cations in equilibrium solution, k is the constant identified as the total exchange capacity, and b_1 and b_2 are constants related to the energy of adsorption of the cations.

H. Jenny (1936) developed a statistical approach for two ions of equal valency. Davis (1945) extended Jenny's equation to include ions of unequal valence. Krishnamoorthy, Davis, and Overstreet (1949) noted similarity between ion exchange and the equilibrium absorptions of mixed gases on surfaces and applied the statistical thermodynamical treatment of Fowler and Guggenheim. Their equation is

$$k_{(A,B)} = \frac{(A)^{r_2}}{(B)^{r_1}} \left(q_1 A + q_2 B + q_3 C \ldots\right)^{r_1 - r_2} \frac{(B)^{r_1}}{(C)^{r_2}}$$

where q = (r 1)/2. They found it to fit both resin and clay exchanger systems for all ion pairs except the hydrogen ion.

Mass action. The reversibility of the ion exchange phenomenon and equivalency of the exchange has lead many to regard ion exchange as following the law of mass action.

Ganssen (1908) was one of the first to apply the law of mass action. Rothmund and Kornfeld (1918) derived a similar relationship to Ganssen. However Kerr (1928) was the first to rigorously apply the mass action law. Kerr assumed that the solid phase behaved as if it were in solution and that it had similar activity.

$$NaZ + K \rightleftharpoons KZ + Na$$

$$K = \frac{(Na)\ (KZ)}{(K)\ (NaZ)}$$

Vanselow (1932) assumed that the two solid phases behave like a continuous solid solution and that the activity of each component is equal to the mole fraction of it in the solid. The equation is the same as Kerr's except that

$$(NaZ) = \frac{NaZ}{NaZ + KZ} \qquad (KZ) = \frac{KZ}{KZ + NaZ}$$

Gapon (1933) assumed both di- and monovalent ions behave similarly on an equivalent basis

$$K = \frac{(Ca^{++})\ (NH_4Z)}{(NH_4^{+})\ (CaZ)}$$

where (Ca^{++}) and (NH_4^+) are expressed on a molar basis and NH_4Z and CaZ on an equivalent basis.

Recently Boyd et al (1948) have tried a more rigorous approach which basicly is an extension of Vanselow's solid solution. They have assumed that the activity coefficient is proportional to the square of the mole fraction. For the exchange

$$A^{r+} + (r^+/r^{+1})\ BR \rightleftharpoons AR + (r^+/r^{+1})\ B^{r+}$$

$$K = \frac{(a_R{}^{r^1+})^{r+/r+1} (N_{AR} + N_{BR})^{r+/r+1} (N_{AR})}{(a_A{}^{r+})\ (N_{BR})^{r+/r+1}}$$

where K is the thermodynamic equilibrium constant, a_B, the activity of ion B, a_A the activity of ion A, r^+, valence of cation a, r^{+1}, the valence of cation B, N_{AR} the number of moles of A in exchanger, N_{BR} the number of moles of B in exchanger. At about the same time Bauman et al (1947) found some difficulties in applying mass action in that the degree of swelling influenced the exchange equilibria. This was verified for anion exchangers by Kunin and Myers (1950). Gregor (1948) approached the problem by rigorous thermodynamical treatment taking into account the change in volume.

KINETICS OF ION EXCHANGE

The kinetics of ion exchange goes back to the time of J. T. Way who noticed that the exchange was rather rapid and only slightly affected by temperature.

Wiegner (1936) decided that the rate of exchange was dependent on the location of the exchange groups. Since the resins are considered to be gel-like particles with the exchange sites at random, there are four steps in the exchange process: (1) The diffusion of ions through the solution to the surface of the exchange particles. (2) The diffusion of these ions through the gel particle. (3) The exchange of these ions with those already in the exchanger, and (4) the diffusion of these latter ions through the particle.

Nachod and Wood (1944), Thomas (1944) and Juda and Carron (Kunin 1950) have considered the rate of exchange to be governed by a bimolecular rate equation. The work of Boyd et al (1947, 1947, 1947, 1948), Bauman and Eichhorn (1947), and Kunin and Myers (1947) and Grossman and Adamson (1952) shows that the process is diffusion controlled. Boyd et al has measured two diffusion rates, one at concentration of 0.003M or less (film diffusion) and one at concentrations of 0.1M or above (particle diffusion). Boyd et al used the shallow bed method first suggested by du Domaine, Swain and Hougen (1943) with radio-isotopes to measure amounts of material.

On the other hand, Vermeulen (1952) has formulated theoretical equations so that a column can be evaluated theorically. Vermeulen's equations are used in the calculations later in this paper and will be discussed there.

Michaels (1952) has developed a simplified method of interpreting kinetic data in fixed-bed ion exchange. His equations give a method of applying the data from small laboratory columns to the design of large ion exchange units.

K. S. Spiegler (1953) is at present studying the diffusion in ion exchange membranes by measuring the spread of a radio-isotope with autoradiographs, or photographic film.

STATEMENT OF PROBLEM AND DEFINITION OF TERMS

Statement of problem. It was the purpose of this work to determine the effect of cross-linkage on the internal diffusion. It has been proposed that the internal diffusion would give some idea of the internal structure of the resin. A resin with a high internal diffusion while having a high external flow would give a narrow zone thereby giving a very good separation.

Since there are two controlling rates, internal and external diffusion, it was necessary to eliminate one. This was done by having a high rate of flow which in effect narrowed the liquid film around the particle and made the internal diffusion the controlling rate. The shape of the zone eluted was measured and a plot of concentration of eluted solution versus volume of solution eluted was made. A relationship is known between the zone width and the rate constant, K_2. The diffusion is proportional to the rate constant; therefore a relationship between the internal diffusion and rate constant can be made qualitatively but not quantitatively.

Definition of terms. When an ion exchange column is run under trace conditions, a small volume of an electrolyte solution is added, i.e. hydrochloric acid, to the column whose resin is in a different form, i.e. NaR or sodium resin. The small volume of HCl will exchange at

the top of the column and create an area of exchanged material called a zone.

i.e. $NaR + HCl \rightleftharpoons HR + NaCl$

A large volume of electrolyte solution i.e. sodium chloride solution, which will change the resin in the zone to it's original form is then added. This solution is called the elution solution or eluting solution. It moves the zone down the column by reversing the reaction and giving HCl which moves to new resin and re-exchanges. Thus it moves the zone down the column. If the diffusion into the resin is high the zone will be narrow but if it is low the zone will widen.

Volume of saturation. This is the initial volume of electrolyte solution added to the column to create a zone. It contains the component which is to be exchanged.

Elution solution. This is an electrolyte solution used to wash (or elute) the volume of saturation (zone).

V_{max}. The volume at which a plot of concentration of eluted solution and volume eluted is at a maximum.

$V_{\frac{1}{2}}$. The volume at which the plot of concentration of solution eluted versus volume eluted is at $\frac{1}{2}$ of the maximum amount.

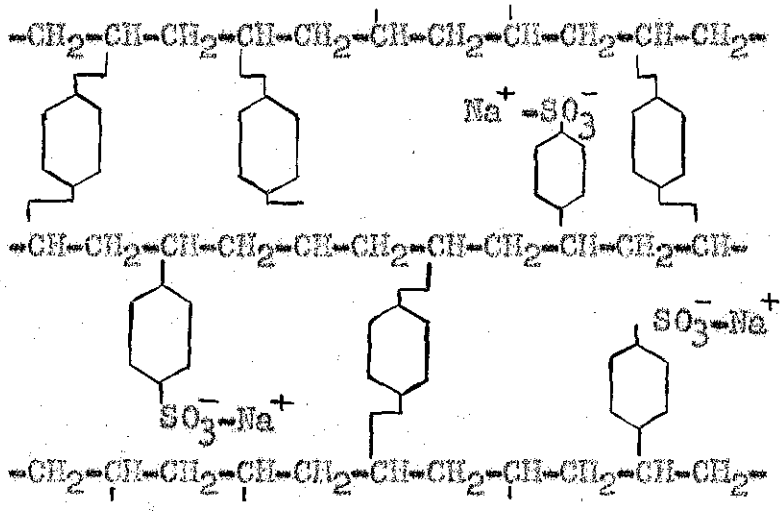
Internal diffusion. It is the diffusion through the ion exchange particle itself or the solution trapped in the particle.

External diffusion. The diffusion through the surface film surrounding the ion exchange particle.

Surface film. Surface film is analogous to the film found when liquid flows in pipes. In steamline flow in a pipe there is a small film which can be considered stationary on the surface of the pipe. The thickness of the film is inversely proportional to the rate of flow.

THE MATERIAL USED DURING EXPERIMENTS

Dowex-50, manufactured by Dow Chemical Company, was used for the exchanging material. It is an aromatic hydrocarbon polymer containing nuclear sulfonic acid groups as the sole ion active group. It is covered by a patent of G. F. D'Alelio. It is made in experimental lots with particle size of 50-100 mesh and with 1%, 2%, 4%, 8%, 12% and 16% cross-linkage. The percentage cross-linkage is varied by the amount of divinyl benzene added during the synthesis. It's basic structure is thought to be



The commercial product, Dowex-50, is available in 20-40 mesh and with 9% cross-linkage. It has a capacity of 4.25 milliequivalents of hydrogen per gram of oven dry resin. It is highly stable over a large range of pH.

PROCEDURE USED TO PREPARE THE RESINS AND FOR THE RUNS

Preparation of resin. The resins were converted into the Na form according to W. K. Lowen et al J. Amer. Chem. Soc. 73, 2660 (1951). Their procedure was:

> SODIUM RESIN.- The pure sodium resin was obtained by maintaining a portion of the hydrogen form in contact with a large excess of sodium chloride solution for two hours. Sodium hydroxide solution was intermittently added to bring the pH of the solution up to that of a saturated sodium chloride solution, where it eventually remained constant.

The resin after being made into the Na form was air dried by putting it in a vacuum desicator and then into an ordinary desicator with calcium chloride. It was left there at least three days before use. When the resins were needed for use they were first weighed and then made into a slurry. This slurry was then poured into the column and washed (or packed) under a pressure of about 5 psi or a vacuum from a water aspirator.

The procedure above was decided upon after some initial trouble. The first procedure tried was to add the dry resin to the column and then wash. It was found that when the resin expanded and the column was put under pressure the tensile strength of the glass was exceeded. It was then that the wire screen (figure II) was added to the apparatus.

The column of ion exchanging material was resting on indentations in the glass tube and glass wool. A nichrome

wire ring covered with glass cloth was first used but it seemed to hold back the flow of liquid therefore it was discarded for the glass wool set-up.

The measurements of the void space of the column, vfe, was done by setting up a buret with glass wool compressed tightly up to the graduations on the tube. The amount of water held by the glass wool was measured a number of times. Then resin was added in the slurry form, and the buret inserted into a filter flask. The filter flask was then attached to a water aspirator and the resin was washed for several minutes. The stop-cock of the buret was closed when the level of the water was at the top of the resin. Then a test tube was placed in the filter flask, and the stop-cock of the buret was opened. The suction was left on until no drops of water could be seen coming through. While the suction was being applied the height of the column was noted on the graduations of the buret. The volume collected was then measured.

Procedure on the runs. The sample or saturation volume, V_{sat}, is placed in funnel, D. Stop-cocks 3 and 2 are opened, and the saturation volume passes into A (see figure II). Stop-cocks 2 and 3 are closed, pressure applied, and 1 and 4 opened. The elution solution is then added to funnel, B. As soon as the saturation volume is below stop-cock 1, it and 4 are closed, and 2 and 3 opened and the elution solution added to A. When the saturation

volume is at the top of the resin, the elution solution is added by closing 2 and 3 and opening 1 and 4. While the solutions are being added, samples have been collected at C in large test tubes. The samples in the test tubes were about 10 mls until near the zone and then a sample of between 2 ml and 4 ml was taken. A stop watch was used to measure the time required to collect the sample; from this the flow rate, F, was determined, also during the elution period the height of the column was measured. These samples were put aside in order and when the run was complete they were titrated with 0.01 N sodium hydroxide with phenolphthalein as the indicator. Blanks were run on different volumes of liquid in the same test tubes which were used in the actual runs (figure I). These blanks were used to correct the runs. The volume of the sample plus the amount of sodium hydroxide was then measured. Then more elution solution was run through the column to make sure the resin was in the Na-form, and another run was started.

Measurement of d_p. Resins of different sizes and cross-linkages were placed in a solution of 1N sodium chloride. This was done to obtain a resin of the same size as was placed in the column. The resin was kept in contact with solution for about 1 hour to complete the adsorption of liquid. The resin was placed in a flat bottom evapor-

ating dish with enough solution to cover it. The resin was spread by shaking until the layer of resin was one particle thick. The resin was then measured with a measuring microscope.

Measurements of d_V. The diameter of the column was measured by the use of vernier calipers. The measurements (see table XII) were taken on a number of pieces of tubing one of which was used to make the column used in the experiment.

FIGURE 1

VOLUME OF BLANK VERSUS NUMBER OF DROPS OF NaOH USED

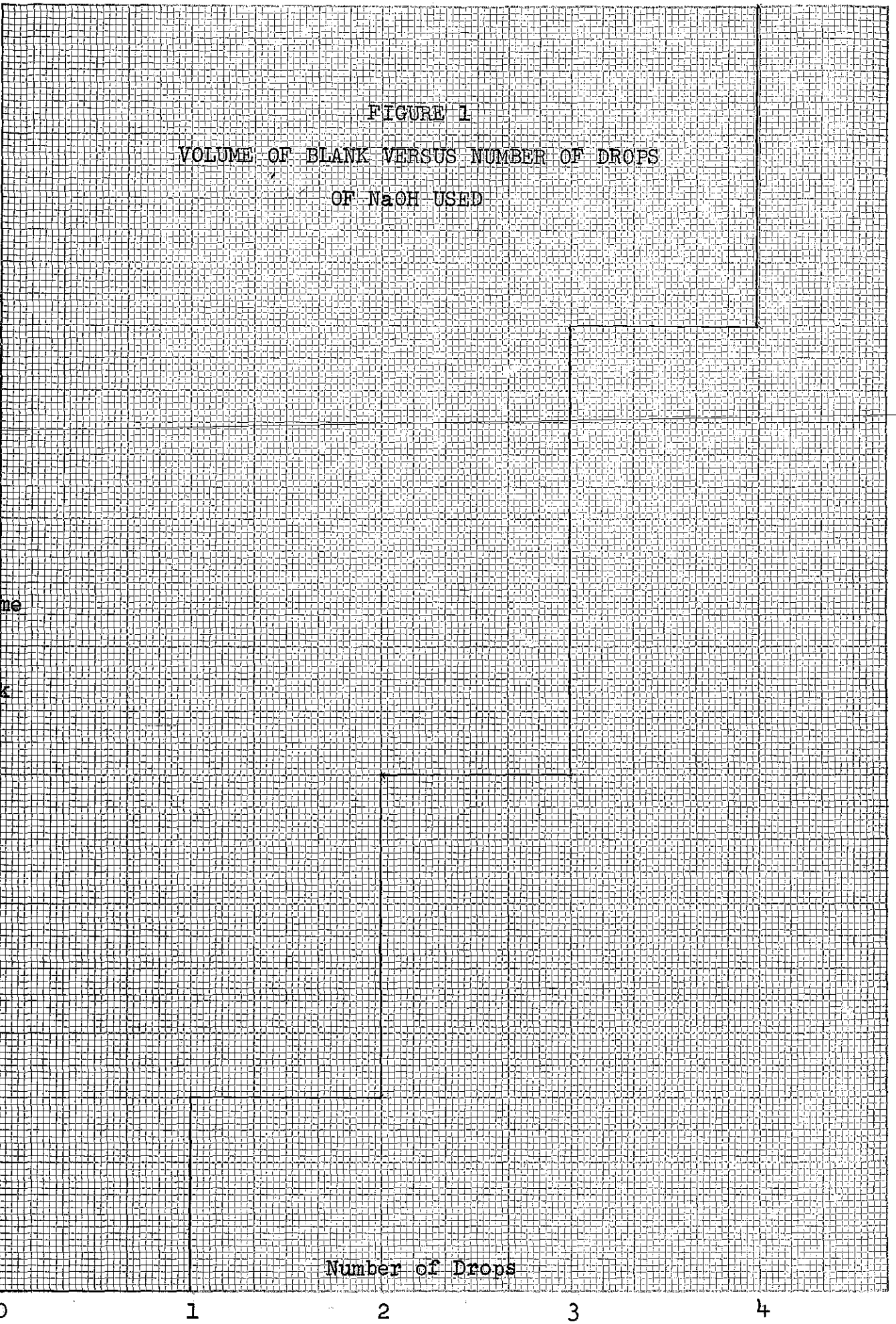
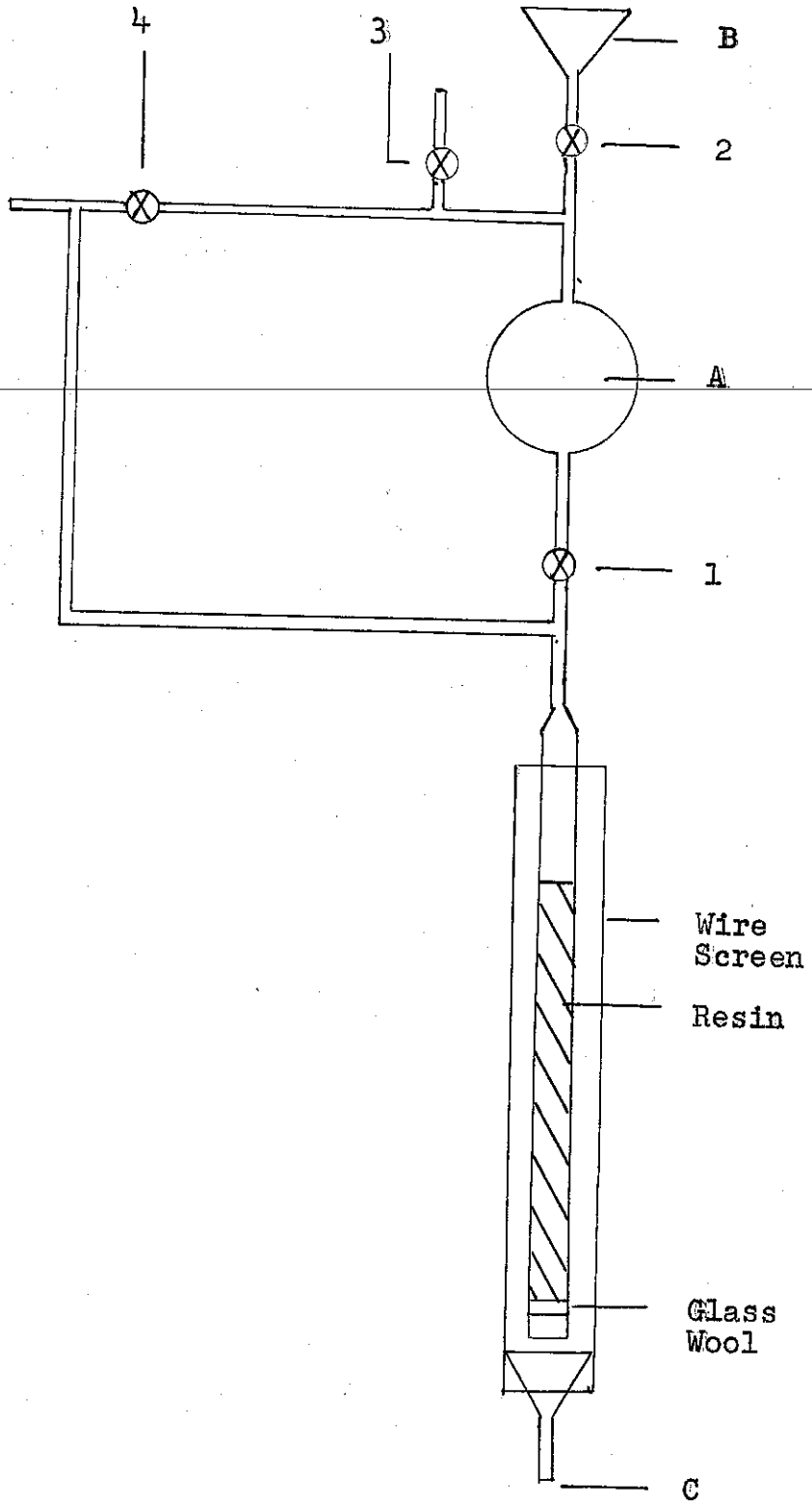


FIGURE 2



THE EQUATIONS USED IN THE CALCULATIONS

It has been found that the best chromatographic separations are achieved when the elution zones are of the Gaussian curve type. The following is a review of the derivation of the equations which are found in Vermeulen and Hiester (1952). We have used their equations for the calculations with the same assumption as theirs. The assumptions are that (1) the quantity of component G, both on the resin and in solution, by exchanging with A, are small enough that the concentration of G can be considered constant, (2) the rate of flow was fast enough to permit the diffusion through the film around the particle to be neglected, (3) the time the saturation volume is in contact with any particle is short.

The quantities measured were:

v = the volume of the bed

fe = the fraction of void space

R = the rate of flow

V_{sat} = the volume of saturating solution

$(c_a)_o$ = the concentration of hydrogen ion in the saturating solution

c_δ = total concentration in eluting solution.

The rate equation

$$\frac{R\partial(q_a/(q_a)_\infty)}{\partial V} = \frac{K_a}{D_a}\left[\frac{c_a}{(c_a)_o}\frac{q_a}{(q_a)_\infty}\right] \qquad (1)$$

in conjunction with a conservation equation, which expresses

the loss of A from the solution and gain of A in the solid,

$$-\left[\frac{\partial c_a}{\partial v}\right]_V = \left[\frac{\partial q_a}{\partial V}\right]_v \quad fe \left[\frac{\partial c_a}{\partial V}\right]_v \qquad (2)$$

has been solved by Thomas (1944).

Since one of the assumptions is that the zone eluted is a Gaussian curve, the Gaussian approximation is used. The equation for the Gaussian approximation is

$$\frac{c'_a}{(c_a)'_o} = \frac{T_a}{2\sqrt{\pi s_a}} \; e^{-\frac{\left[t'_a - (s_a - \frac{1}{2} T_a)\right]^2}{4 s_a}} \qquad (3)$$

where

$$s_a = \frac{K_a vfe}{R} \qquad (4) \qquad t'_a = \frac{K_a}{D_a} \; \frac{V' - vfe}{R} \qquad (5)$$

The solution of the rate equation (1) and conservation equation (2) gave these two parameters, s_a and T_a. In these equations Ka is the rate constant, vfe is the void space in the column, R is the rate of flow, and s_a is called the column capacity parameter, D_a is the distribution ratio, V' is the volume which has been eluted and t'_a is the solution capacity parameter. The Gaussian curve is acquired from a plot of $(c'_o/c'_o)_a$ versus the volume eluted. From this plot which assumes that the curve is Gaussian one obtains the following equations:

$$\text{(Volume at Maximum)} = vfe(1 + D'_a) - \frac{V_{sat}}{2} \; \frac{D'_a}{D_a} \qquad (6)$$

$$\left[\frac{c_a}{(c_a)_o}\right] \text{at maximum} = \frac{V_{sat}}{2 D'_a} \sqrt{\frac{K_a}{\pi R \; vfe}} \qquad (7)$$

At a maximum the $t'_{a(max)} = (s_a - \frac{1}{2}T_a)$ and the half height to the maximum of t_a would be $t'_{\frac{1}{2}} - t'_{max}$. At the half height width in t'_a becomes $t'_{\frac{1}{2}} - (s_a - \frac{1}{2}T_a)$. Therefore equation (3) becomes

$$1/2 = e^{-\frac{\left[t_{\frac{1}{2}} - (s_a - T_a)\right]^2}{4\, s_a}} \qquad (8)$$

Solving for s_a one obtains

$$s_a = \frac{\left[t'_a - (s_a - \frac{1}{2}T_a)\right]^2}{4 \ln 2} \qquad (9)$$

By substitution of one of the original parameters, t'_a (equation 5)

$$s_a = \left[\frac{K_a}{D'_a R}\right]^2 \frac{(V - V_{max})^2}{4 \ln 2} \qquad (10)$$

By the substitution of s_a (equation (4)) and solving for K_a one obtains

$$K_a = \frac{4 \ln 2\, R\, vfe\, (D'_a)^2}{(V - V_{max})^2}$$

Solving equation (6) for D'_a and assuming trace conditions and substitution in equation (6) of

$$\frac{D_a}{D'_a} = \left[\frac{c'_o}{c_o}\right]^{4/r}$$

and by substitution of equation (6)

$$K_a = \frac{4 \ln 2\, R}{vfe} \frac{V_{max} - vfe\, (c'_o/c_o)^{4/r}\, (V_{sat}/2)}{V_{\frac{1}{2}} - V_{max}} \qquad (11)$$

The equation for the void fraction of the column was

$$fe = \frac{\text{total milliliters collected}}{\text{total volume of column}} \qquad (12)$$

This equation was used since the total milliliters collected and the volume of the column were measured directly.

TABLE I

SUMMARY OF CALCULATED VALUES OF FE

% Cross-linkage	Mesh	fe	feS
2	40 - 60	0.2134± .0036	0.1683
4	40 - 60	0.2559±0.0074	0.2018
4	60 - 80	0.2925±0.0113	0.2306
8	60 - 80	0.2833±0.0123	0.2234
16	60 - 80	0.2951±0.0081	0.2327

TABLE II

MEASUREMENT OF HOLD UP VOLUME OF GLASS WOOL

Run No.	M1	M1	M1 - M1	$(M1 - M1)^2$
1	45.1-49.3	4.2	.2	0.04
2	40.3-45.1	4.9	.4	0.16
3	36.0-40.3	4.3	.1	0.01
4	31.6-36.1	4.5	.1	0.01
5	44.7-49.1	4.4	.0	0.00
6	40.3-44.6	4.3	.1	0.01
7	44.6-49.0	4.4	.0	0.00
	MEAN	4.4	TOTAL	0.23

Hold up volume of glass wool = 4.4 ± .07

TABLE III

MEASUREMENT OF MILLILITERS OF VWE

2% (40-60) Resin

Weight of Resin 10.0084 gms

Run No.	Ml	Ml	Ml - Ml	$(Ml - Ml)^2$	V. of Column	
1	35.7-44.5	8.8	0.06	0.0036	20.8	
2	27.1-36.2	9.1	0.24	0.0576		
3	18.5-27.1	8.6	0.26	0.0676	21.0	
4	34.9-43.7	8.8	0.06	0.0036		
5	25.8-34.8	9.0	0.14	0.0196	20.9	
	MEAN	8.86	TOTAL	0.1520	MEAN 20.9	.04

Milliliters collected = $8.86 \pm .025$

Milliliters of glass wool = 4.4 ± 0.07

Total Milliliters collected = $4.46 \pm .0743$

TABLE IV

MEASUREMENT OF MILLILITERS OF VFE

4% (40-60 Mesh) Resin

Weight of Resin 10.3473 gms

Run No.	Ml	Ml	Ml - Ml	$(Ml - Ml)^2$	V. of Column
1	38.1-47.2	9.1	.18	0.0324	17.6
2	29.0-38.0	9.0	.08	0.0064	
3	20.5-29.0	8.5	.42	0.176	17.8
4	23.5-32.3	8.8	.12	0.0144	17.6
5	14.2-23.4	9.2	.28	0.0784	
	MEAN	8.92	TOTAL	0.3075	MEAN 17.66

Milliliters Collected = 8.92 ± .11

Milliliters of Glass Wool = 4.4 ± 0.07

Total Milliliters Collected 4.52 ± .13

TABLE V

MEASUREMENT OF MILLILITERS OF VFE

4% (60-80 Mesh) Resin

Weight of Resin 8.5214 gms

Run No.	Ml	Ml	Ml - Ml	$(Ml - Ml)^2$	V. of Column	
1	25.0-34.8	9.8	0.6	0.36	16.8	
2	15.2-24.9	9.7	0.4	0.16		
3	13.2-22.1	8.9	0.4	0.16		
4	22.1-31.5	9.4	0.1	0.01	16.7	
5	19.6-28.5	8.9	0.4	0.16		
	MEAN	9.3 .18	TOTAL	0.85	MEAN 16.75	.035

Milliliters Collected = 9.3 ± .18

Milliliters of Glass Wool = 4.4 ± .07

Total Milliliters Collected = 4.9 ± .19

TABLE VI

MEASUREMENTS OF MILLILITERS OF VFE

8% (60-80 Mesh) Resin

Weight of Resin 8.1073

Run No.	Ml	Ml	Ml - Ml	$(Ml - Ml)^2$	V. of Column	
1	39.7-47.6	7.9	0.16	0.0256	11.6	
2	32.1-39.4	7.3	0.44	0.1936		
3	38.7-46.8	8.1	0.39	0.1521		
4	30.9-38.7	7.8	0.06	0.0036	11.7	
5	23.3-30.9	7.6	0.14	0.0196		
	MEAN	7.74	TOTAL	0.3945	MEAN	11.65 .035

Milliliters Collected = 7.74 ± .125

Milliliters of Glass Wool = 4.4 ± .07

Total Milliliters Collected = 3.3 ± .143

TABLE VII

MEASUREMENT OF MILLILITERS OF VFE

16% (60 - 80 Mesh) Resin

Weight of Resin 7.6748 gms

Run No.	Ml	Ml	Ml - Ml	$(Ml - Ml)^2$	V. of Column
1	Void				
2	30.1-38.1	8.0	0.00	0.00	12.2
3	22.3-30.1	7.8	0.20	0.04	
4	14.1-22.3	8.2	0.20	0.04	12.2
5	40.0-48.2	8.2	0.20	0.04	12.2
	MEAN	8.0	TOTAL	0.12 MEAN	12.2 0

Milliliters Collected = 8.00 ± .07

Milliliters of Glass Wool = 4.4 ± .07

Total Milliliters Collected = 3.6 ± .099

ORIGINAL DATA

A plot of the concentration versus volume eluted is used to determine the V_{max} and $V_{\frac{1}{2}}$. These plots were made on probability paper because the paper gives a straight line with a Gaussian curve. The V_{max} is 50% on the paper because it is divided into the summation of the area under the curve against a straight graph. $V_{\frac{1}{2}}$ is the point of 11.9% and 88.1% of the area under the curve.

TABLE VIII

DATA COLLECTED FROM RUNS ON 2% CROSS-LINKAGE

Constants are d_w = 1.002 cm, c_o = 1.00 N sodium chloride, and d_p = 0.0274 cm.

Run	h	V_{sat}	Resin, gms	R	V_{max}	$V_{max}-V_{\frac{1}{2}}$
a	20.5	5	10	.522	50	8
b	18	5	10	.378	44	5
c	18	8	10	.421	39	5
d	14	6	8	.4205	47	5.5
e	14	6	8	.411	36.5	4
f	23	6	10	.307	41	5
g	16	6	10	.254	50.5	6
h	16	6	10	.261	49.5	6

TABLE IX

DATA COLLECTED FROM RUNS ON 4% CROSS-LINKAGE

Constants are c_o = 1N sodium chloride, dw = 1.002, and dp = 0.0213.

Run	h	V_{sat}	Resin, gms	R	V_{max}	$V_{max}-V_{\frac{1}{2}}$
a	19.5	8	10	.328	60	5
b	21.5	8	10	.294	55	5
c	19	6	10	.221	57	5
d	Void					
changes from 0.0213 cm to 0.0274 cm.						
e	23	4	10	.548	57	7
f	20	4	10	.297	48	10
g	19	10	10	.361	53	10

TABLE X

DATA COLLECTED FROM RUNS ON 8% CROSS-LINKAGE

The constants are $d_p = 0.0213$, $d_w = 1.002$, and c_o = 1 N sodium chloride.

Run	h	V_{sat}	Resin, gms	R	V_{max}	$V_{max}-V_{\frac{1}{2}}$
a	17.5	4	10	.284	59	9.5
b	17.5	6	10	.352	56	7.5
c	17.5	8	10	.286	63.5	10
d	17.5	10	10	.214	61	8.5
e	20	4	10	.271	36	8.0
f	20	6	10	.257	45	10
g	19.5	8	10	.189	46	8.5

TABLE XI

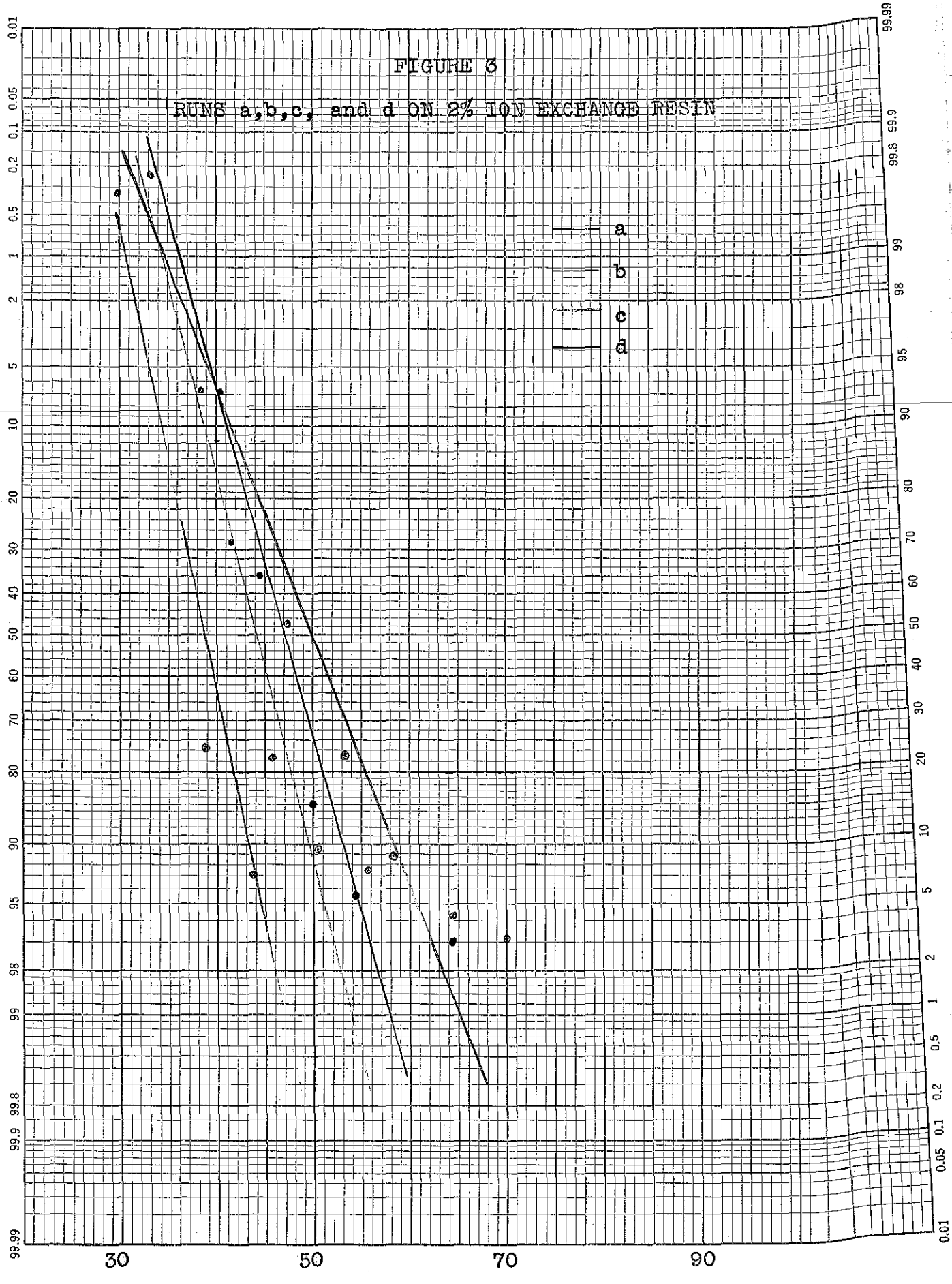
DATA COLLECTED FROM RUNS ON 16% CROSS-LINKAGE

The constants are dp = 0.0213, dw = 1.002 and c_o is 1 N sodium chloride.

Run a to c	h Void	V_{sat}	Resin, gms	R	V_{max}	$V_{max}-V_{\frac{1}{2}}$
d	21	10	10	.242	64	26
e	21	10	10	.242	67	15
f	21	10	10	.341	65	18
g	Void					
h	21	10	10	.513	64	17
i	17	10	8	.804	60	24
j	17	10	8	.373	52.5	15
k	17	10	10	.352	54.5	14.5
l	17	10	10	.673	45.5	18
m	17	8	10	.622	54	14.5
n	Void					
o	Void					
p	20	15	10	.221	62	15
q	20	6	10	.247	62.5	15

FIGURE 3

RUNS a, b, c, and d ON 2% ION EXCHANGE RESIN



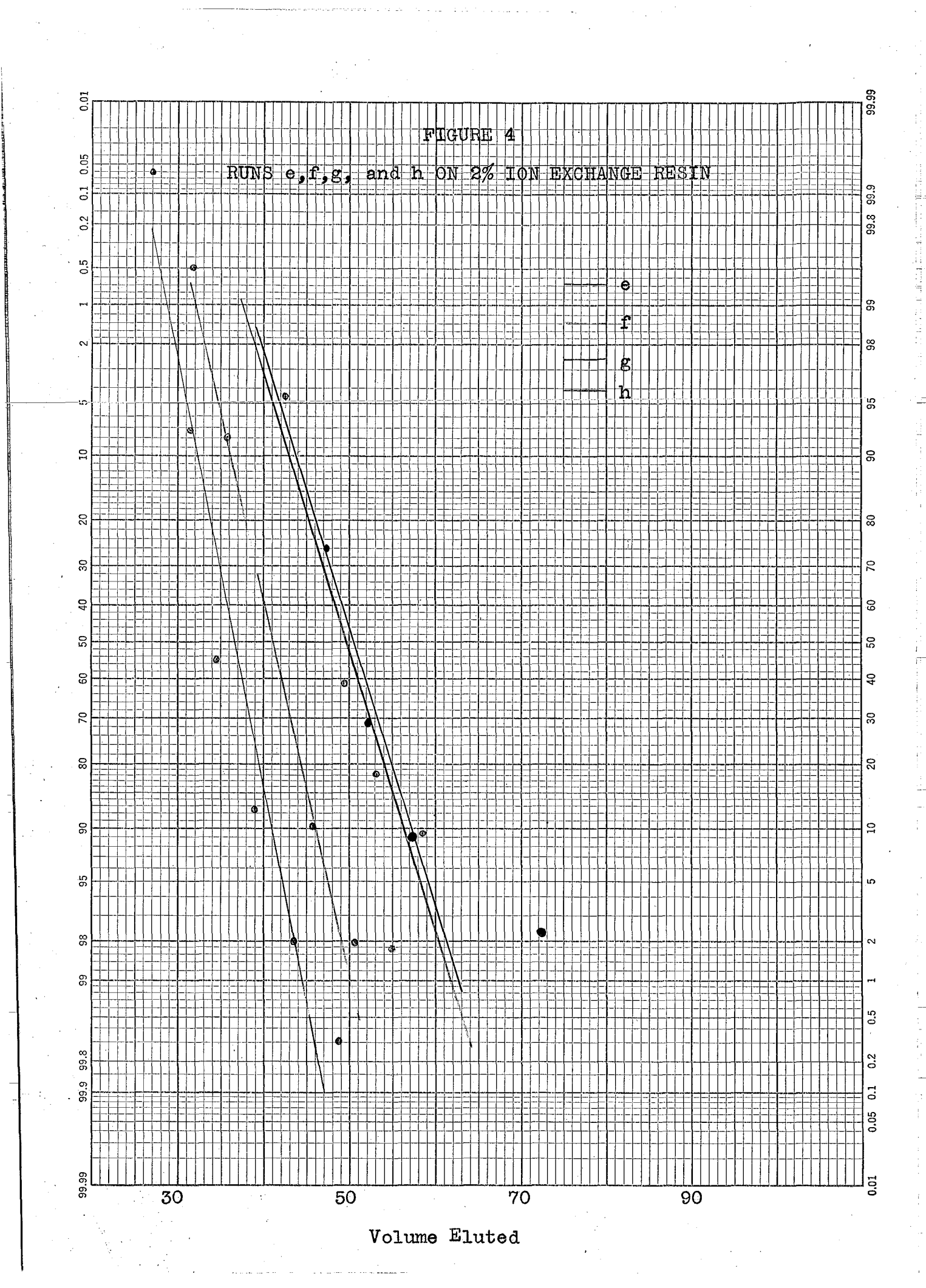
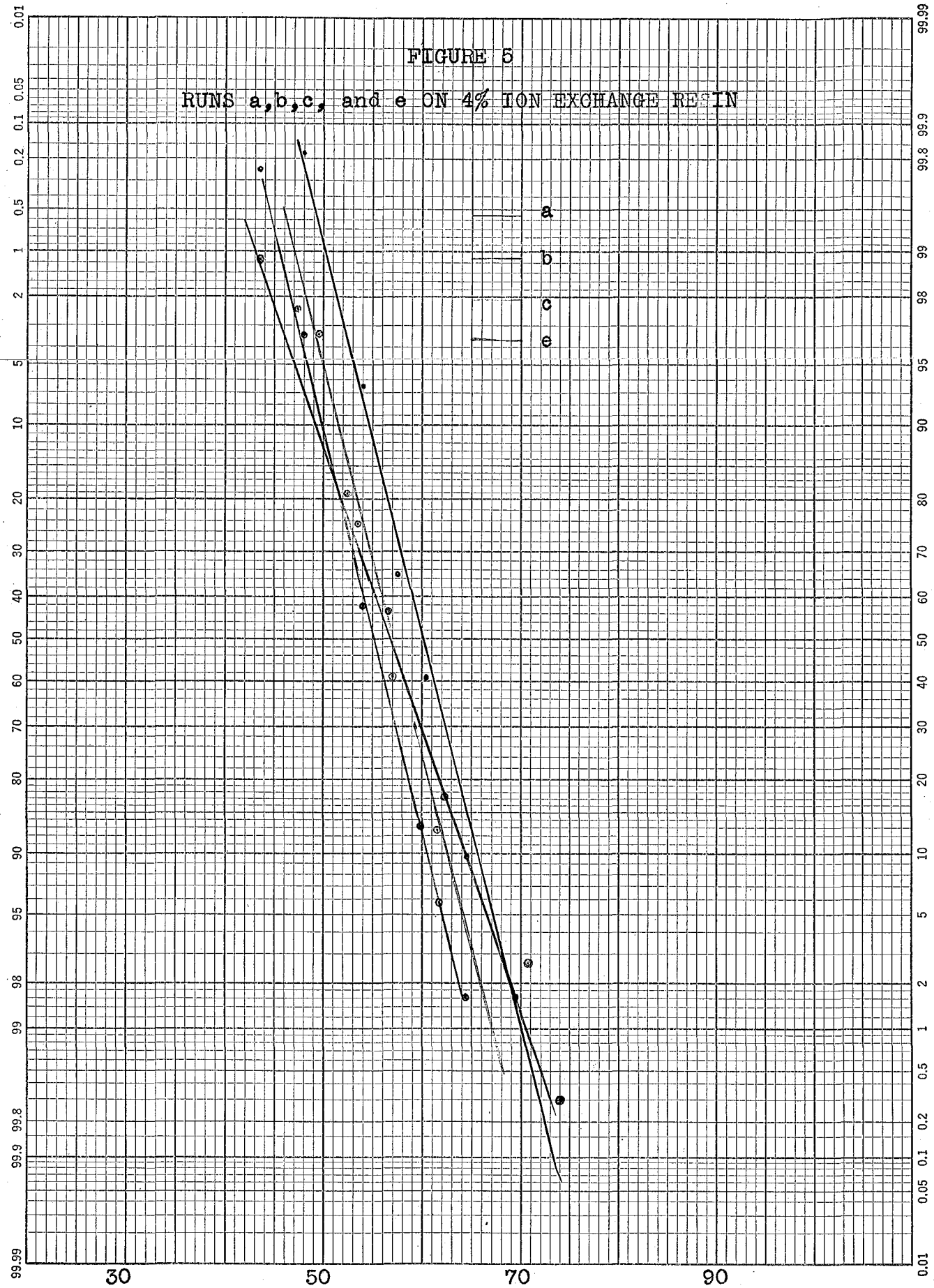


FIGURE 4
RUNS e,f,g, and h ON 2% ION EXCHANGE RESIN
e
f
g
h
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
30
50
70
90
Volume Eluted

FIGURE 5

RUNS a, b, c, and e ON 4% ION EXCHANGE RESIN



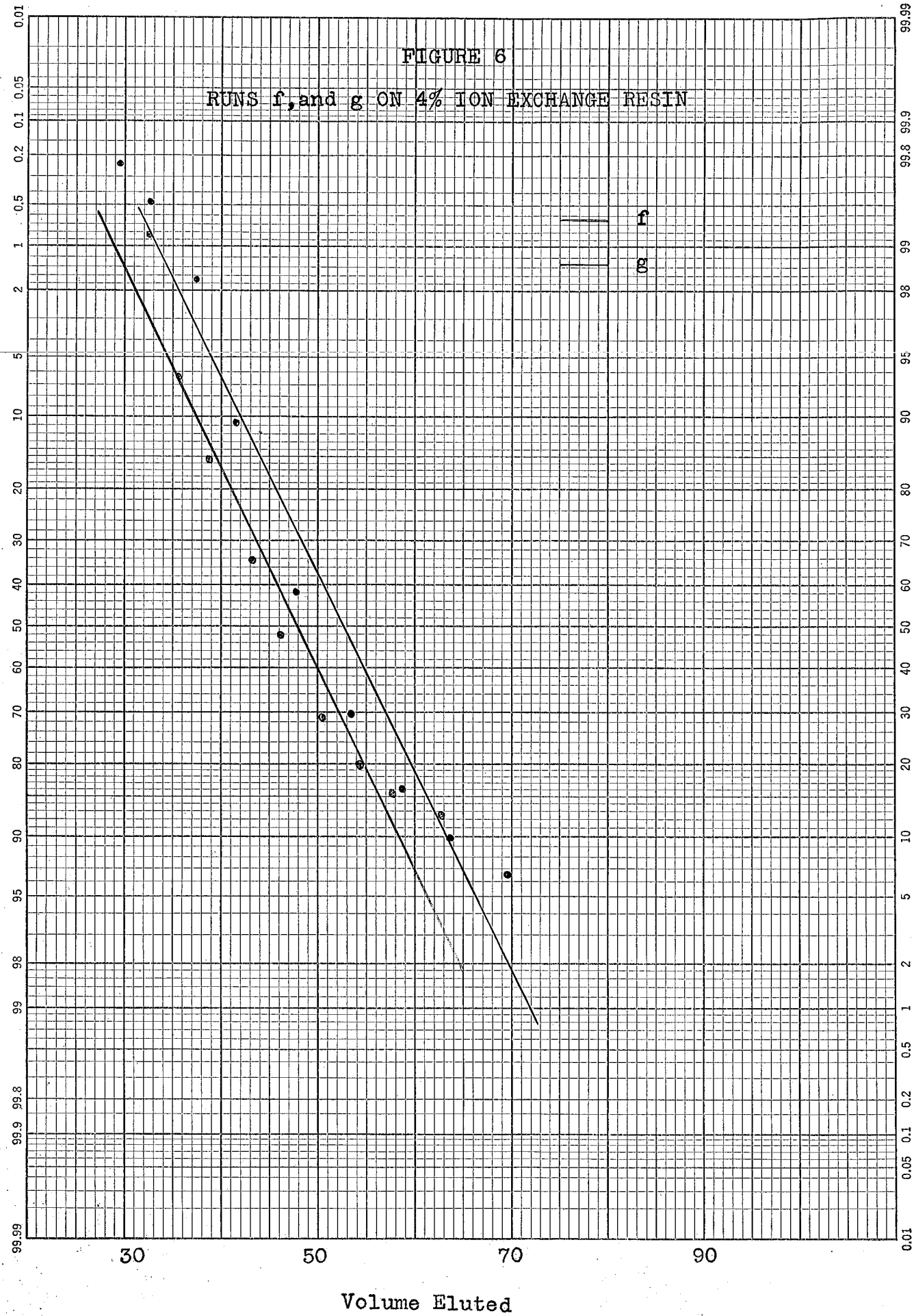
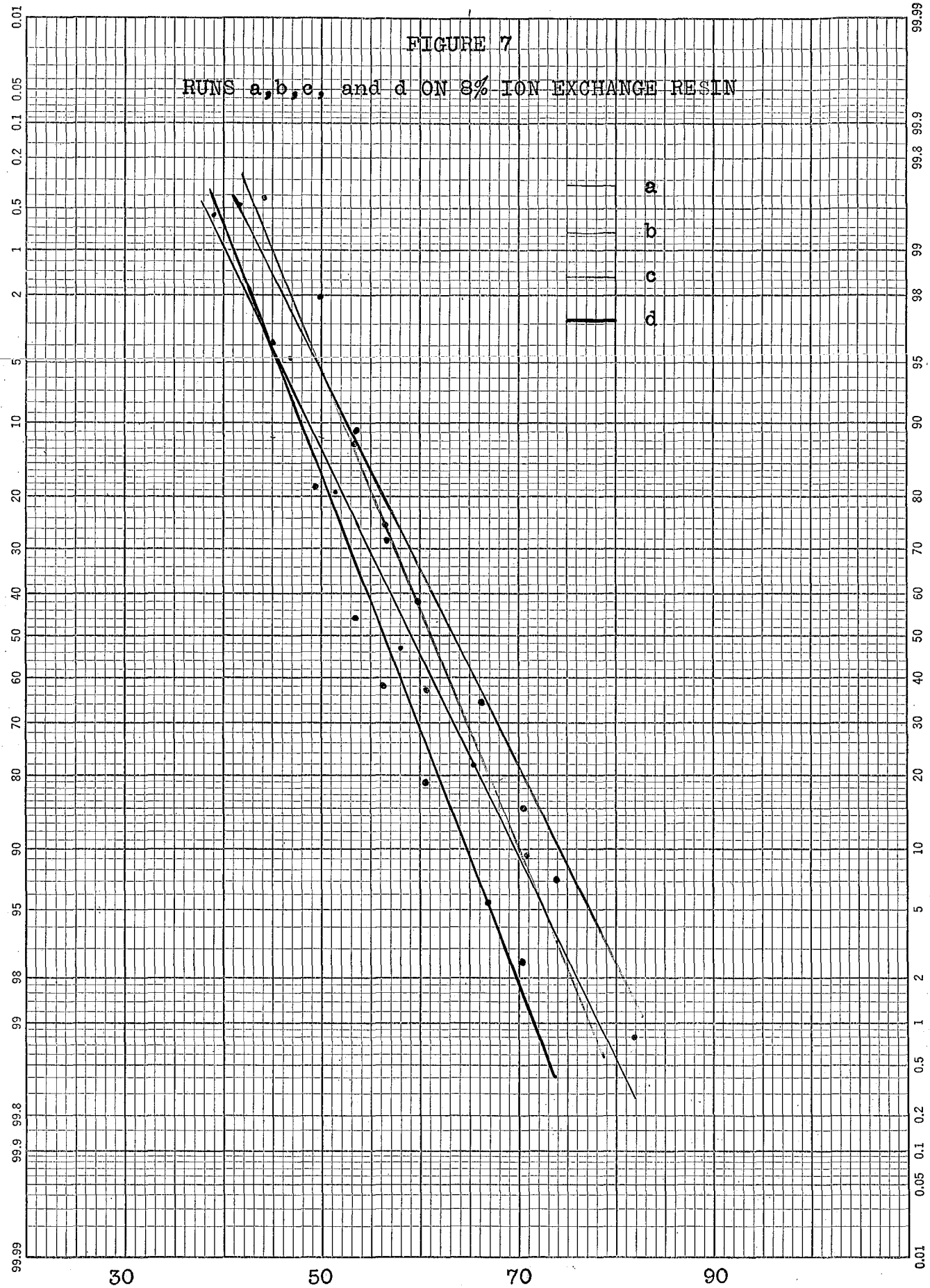


FIGURE 6
RUNS f, and g ON 4% ION EXCHANGE RESIN
f
g
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
30
50
70
90
Volume Eluted

FIGURE 7

RUNS a, b, c, and d ON 8% ION EXCHANGE RESIN



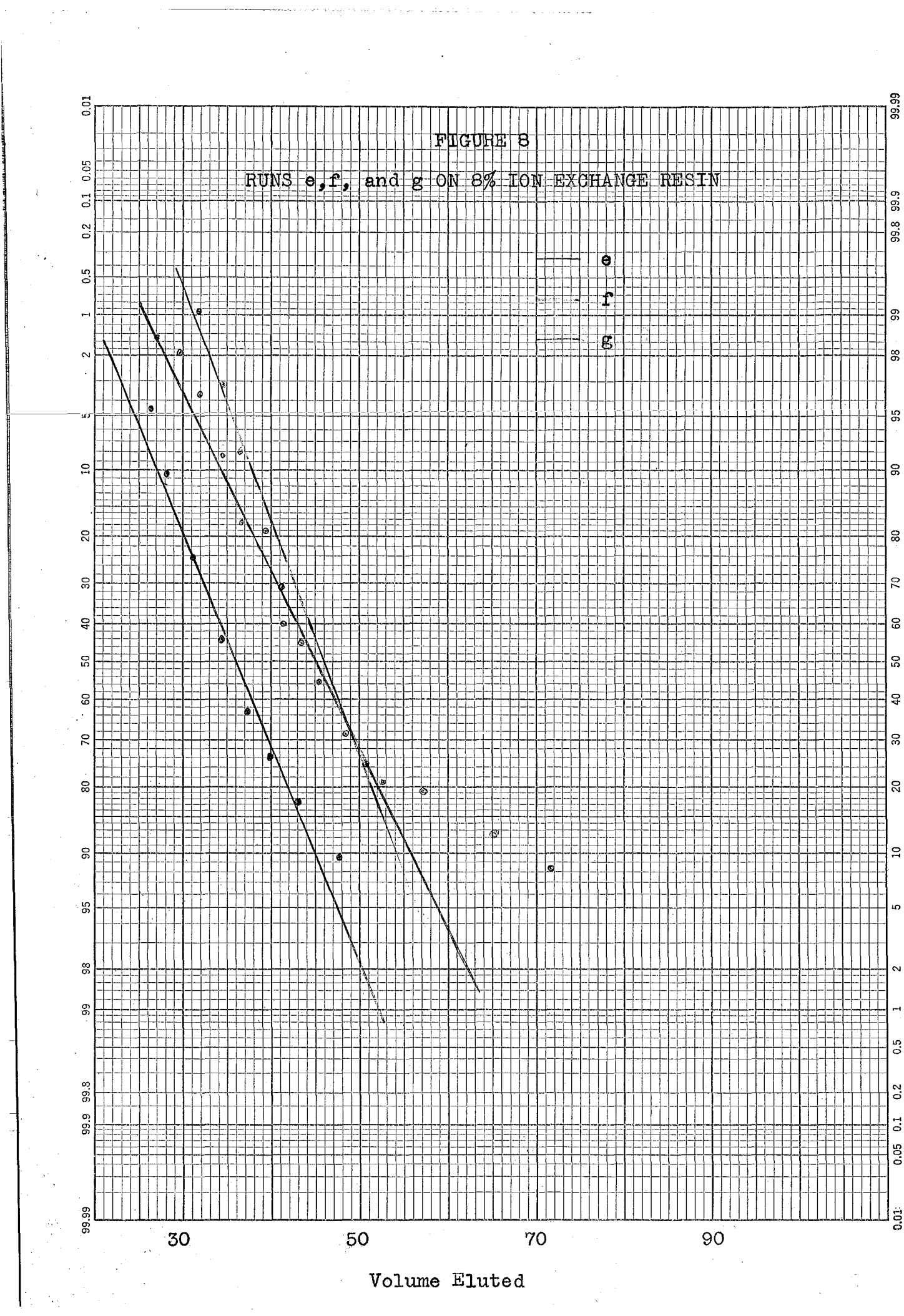


FIGURE 8
RUNS e, f, and g ON 8% ION EXCHANGE RESIN
e
f
g
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
30
50
70
90
Volume Eluted

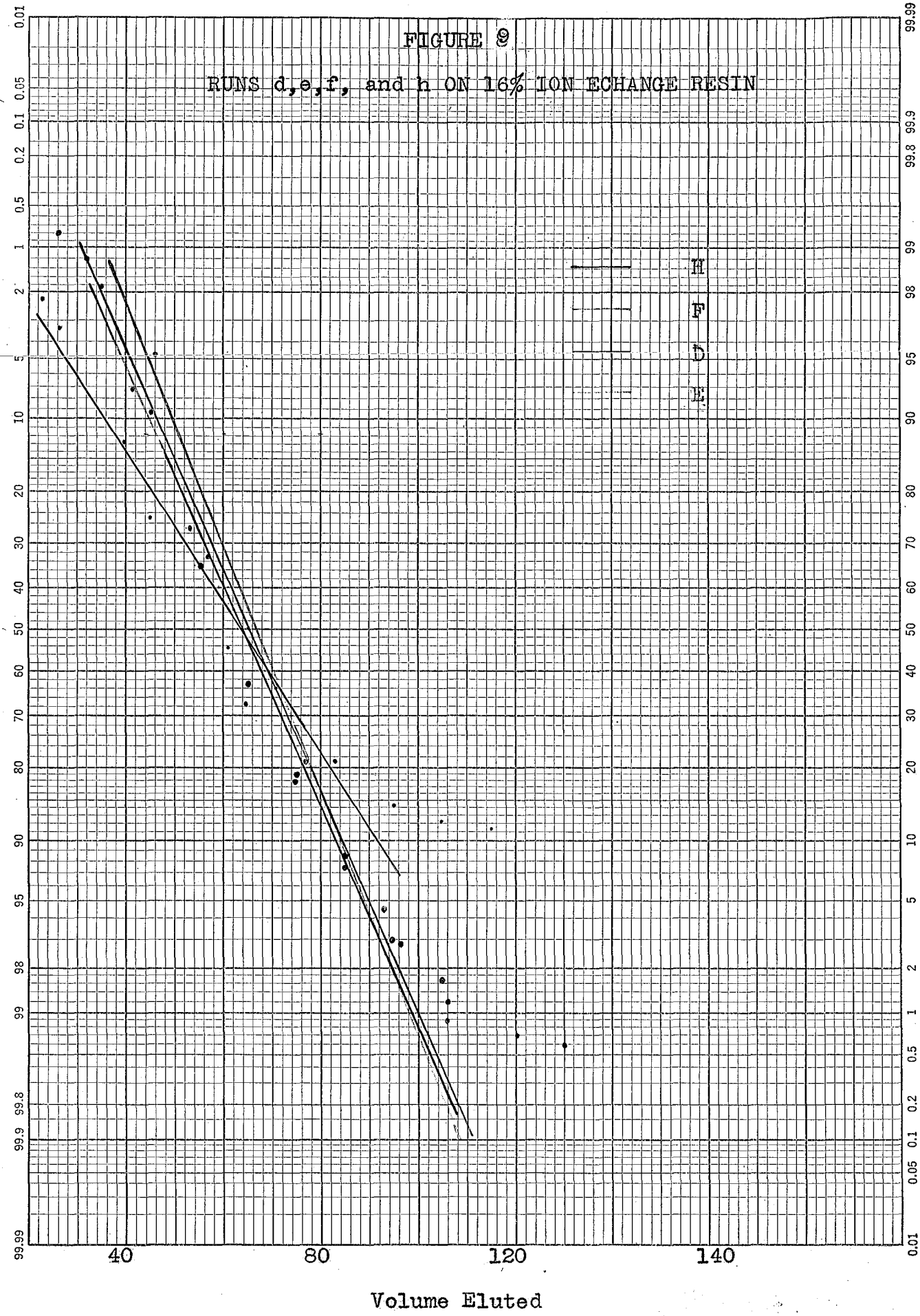
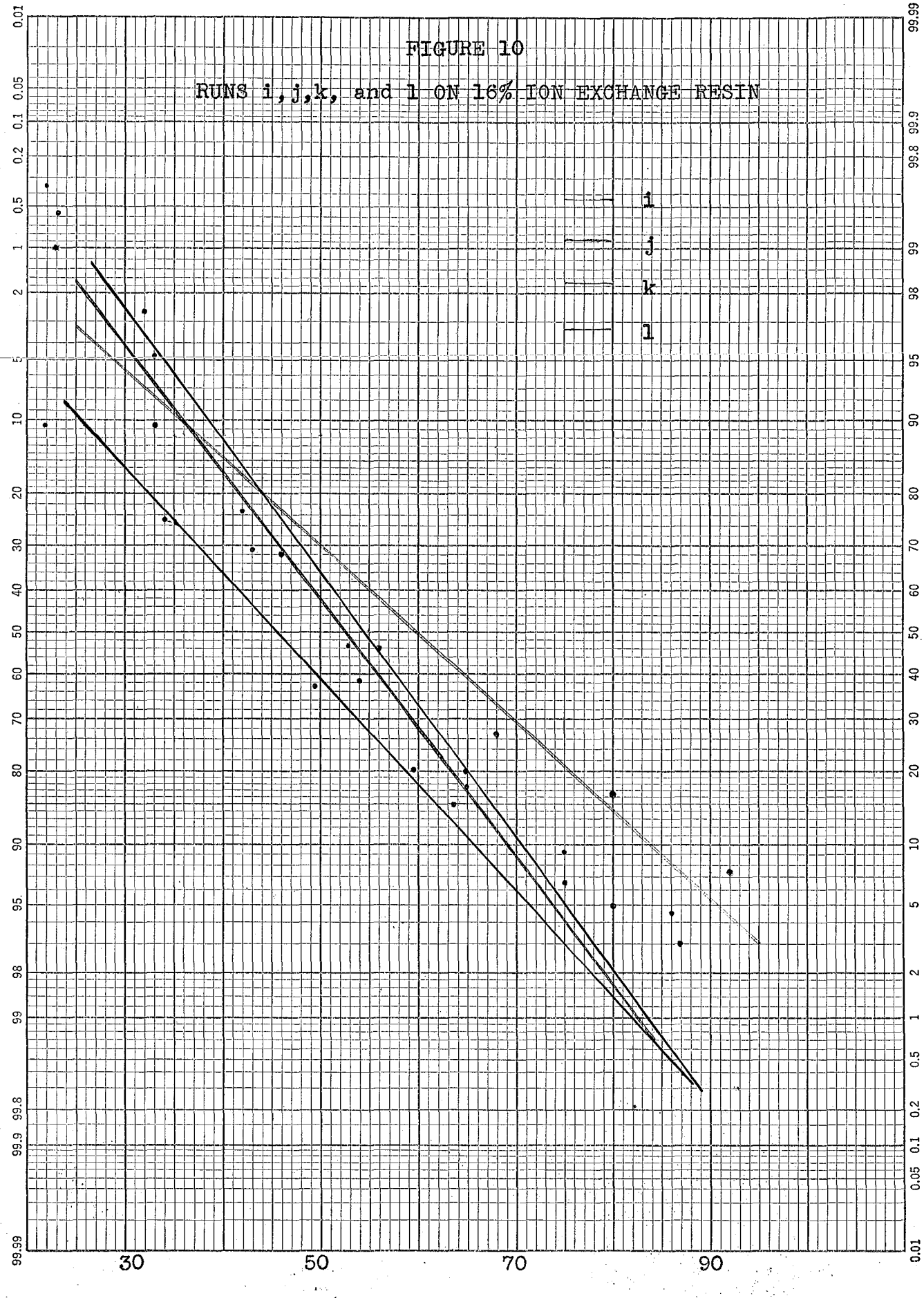


FIGURE 9
RUNS d,e,f, and h ON 16% ION ECHANGE RESIN
H
F
D
E
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
40
80
120
140
Volume Eluted

FIGURE 10

RUNS i, j, k, and l ON 16% ION EXCHANGE RESIN



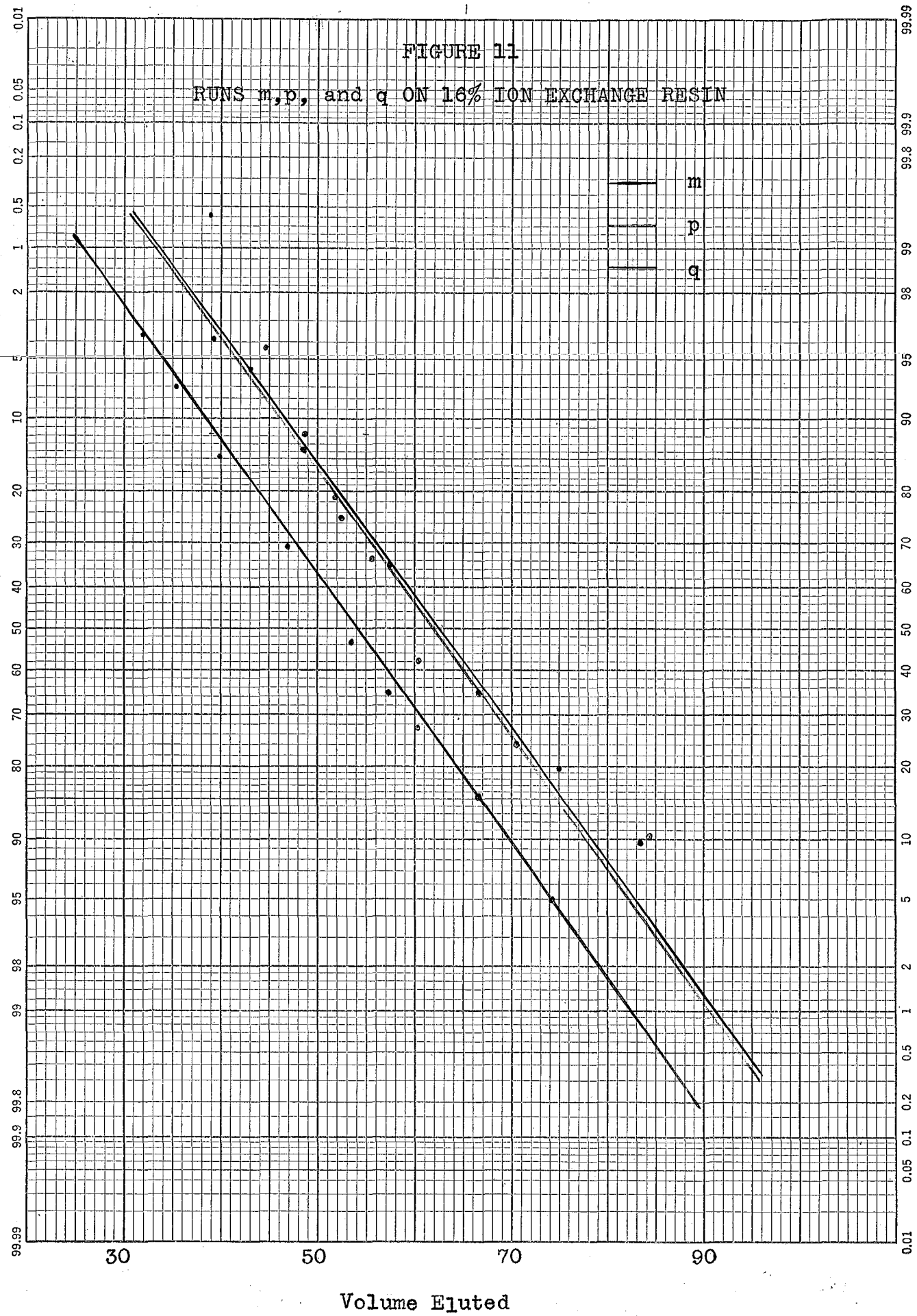


FIGURE 11
RUNS m, p, and q ON 16% ION EXCHANGE RESIN
m
p
q
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
30
50
70
90
Volume Eluted

TABLE XII

MEASUREMENTS OF d_w, the COLUMN DIAMETER

Measurement	d_w	$(d_w - d_{w(mean)})$	$(d_w - d_{w(mean)})^2$
1	1.01	0.008	0.000064
2	1.00	0.002	0.000004
3	1.00	0.002	0.000004
4	1.01	0.008	0.000064
5	1.02	0.018	0.000324
6	1.02	0.018	0.000324
7	0.99	0.0012	0.00000144
8	1.00	0.002	0.000004
9	1.00	0.002	0.000004
10	0.99	0.0012	0.00000144
11	1.00	0.002	0.000004
12	0.99	0.0012	0.00000144
Mean	1.002	Total	0.00077932

d_w, Column diameter = 1.002 ± 0.002

TABLE XIII

MEASUREMENTS OF d_p IN 2% RESIN (40-60 MESH)

Run	Reading(1)	Reading(2)	d_p	$d_p - d_{p(mean)}$	$(d_p - d_{p(mean)})^2 \times 10^4$
1	8.098	8.132	.034	.0061	.3721
2	8.232	8.264	.032	.0041	.1681
3	8.362	8.380	.018	.0099	.9801
4	8.414	8.434	.020	.0079	.6241
5	8.476	8.504	.028	.0019	.0361
6	8.546	8.580	.034	.0061	.3721
7	8.588	8.620	.038	.0119	1.4161
8	Void				
9	8.792	8.816	.024	.0039	.1521
10	8.850	8.888	.038	.0119	1.4161
11	8.940	8.970	.030	.0021	.0441
12	9.000	9.012	.012	.0159	2.5281
13	9.058	9.088	.030	.0021	.0441
14	9.136	9.168	.032	.0041	.1681
15	9.182	8.214	.032	.0041	.1681
16	9.340	9.350	.010	.0179	3.2041
17	8.414	8.454	.040	.0121	1.4641
18	8.504	8.538	.034	.0061	.3721
19	8.612	8.636	.024	.0061	.3721
20	8.792	8.812	.020	.0079	.6241
		Mean	.0279	Total	14.52

$d_p = 0.0279 \pm 0.0019$

TABLE XIV

MEASUREMENTS OF d_p IN 4% RESIN (40-60 MESH)

Run	Reading (1)	Reading (2)	d_p	$d_p - d_{p(mean)}$	$(d_p - d_{p(mean)})^2 \times 10^4$
1	8.332	8.296	.036	.0034	.1156
2	8.268	8.232	.036	.0034	.1156
3	8.440	8.472	.032	.0006	.0036
4	8.458	8.424	.034	.0014	.0196
5	8.496	8.528	.032	.0006	.0036
6	8.562	8.596	.034	.0014	.0196
7	8.620	8.648	.028	.0046	.2116
8	8.648	8.682	.034	.0014	.0196
9	8.690	8.718	.028	.0046	.2116
10	8.738	8.766	.028	.0046	.2116
11	8.806	8.834	.028	.0046	.2116
12	8.880	8.912	.032	.0006	.0036
13	8.926	8.964	.038	.0054	.2916
14	9.000	9.028	.028	.0046	.2116
15	9.064	9.096	.032	.0006	.0036
16	9.108	9.142	.034	.0014	.0196
17	9.170	9.200	.030	.0026	.0676
18	9.212	9.248	.036	.0034	.1156
19	9.280	9.320	.040	.0074	.5476
20	9.344	9.376	.032	.0006	.0036
		Mean	.0326	Total	2.408

$d_p = 0.0326 \pm 0.00077$

TABLE XV

MEASUREMENTS OF d_p IN 4% RESIN (60-80 MESH)

Run	Reading (1)	Reading (2)	d_p	$d_p - d_{p(mean)}$	$(d_p - d_{p(mean)})^2 \times 10^4$
1	7.996	8.020	.024	.0003	.0009
2	8.028	8.050	.022	.0017	.0289
3	8.108	8.134	.026	.0023	.0529
4	8.146	8.170	.024	.0003	.0009
5	8.196	8.220	.024	.0003	.0009
6	8.236	8.260	.024	.0003	.0009
7	8.286	8.308	.022	.0017	.0289
8	8.316	8.340	.024	.0003	.0009
9	8.362	8.384	.022	.0017	.0289
10	8.472	8.496	.024	.0003	.0009
11	8.532	8.556	.024	.0003	.0009
12	8.572	8.588	.016	.0077	.5929
13	8.590	8.608	.018	.0057	.3249
14	8.624	8.646	.022	.0017	.0289
15	8.628	8.652	.024	.0003	.0009
16	8.668	8.694	.026	.0023	.0529
17	8.700	8.726	.026	.0023	.0529
18	8.746	8.780	.034	.0103	1.0609
19	8.832	8.852	.020	.0037	.1369
20	8.888	8.916	.028	.0043	.1849
		Mean	.0237	Total	2.582

$d_p = 0.0237 \pm 0.0008$

TABLE XVI

MEASUREMENTS OF d_p IN 8% RESIN (60-80 MESH)

Run	Reading(1)	Reading(2)	d_p	$d_p - d_{p(mean)}$	$(d_p - d_{p(mean)})^2 \times 10^4$
1	7.796	7.828	.032	.009	.81
2	7.822	7.850	.018	.005	.25
3	7.848	7.868	.020	.003	.09
4	7.866	7.886	.020	.003	.09
5	7.908	7.932	.024	.001	.01
6	7.950	7.976	.026	.003	.09
7	8.008	8.028	.020	.003	.09
8	8.062	8.084	.022	.001	.01
9	8.090	8.116	.026	.003	.09
10	8.150	8.176	.026	.003	.09
11	8.176	8.200	.024	.001	.01
12	8.220	8.242	.022	.001	.01
13	8.246	8.268	.022	.001	.01
14	8.264	8.280	.016	.007	.49
15	8.292	8.316	.024	.001	.01
16	8.316	8.340	.024	.001	.01
17	8.340	8.362	.022	.001	.01
18	8.400	8.430	.030	.007	.49
19	8.444	8.464	.020	.003	.09
20	8.728	8.750	.022	.001	.01
		Mean	.023	Total	2.76

$d_p = 0.023 \pm 0.00083$

TABLE XVII

MEASUREMENTS OF d_p IN 16% RESIN (60-80 MESH)

Run	Reading(1)	Reading(2)	d_p	$d_p-d_{p(mean)}$	$(d_p-d_{p(mean)})^2 \times 10^4$
1	8.080	8.100	.020	.0039	.1521
2	8.168	8.192	.024	.0001	.0001
3	8.290	8.318	.028	.0041	.1681
4	8.748	8.780	.032	.0081	.6561
5	8.794	8.816	.020	.0039	.1521
6	8.840	8.856	.016	.0079	.6241
7	8.864	8.876	.012	.0119	1.4161
8	8.878	8.896	.018	.0059	.3481
9	8.900	8.918	.018	.0059	.3481
10	8.960	8.980	.020	.0039	.1521
11	8.980	9.000	.020	.0039	.1521
12	9.220	9.236	.016	.0079	.6241
13	8.500	8.480	.020	.0039	.1521
14	8.132	8.096	.036	.0121	1.4641
15	8.120	8.092	.028	.0041	.1681
16	8.000	8.036	.036	.0121	1.4641
17	8.050	8.084	.034	.0101	1.0201
18	8.130	8.164	.034	.0101	1.0201
19	8.252	8.284	.032	.0081	.6561
20	8.300	8.314	.014	.0099	.9801
		Mean*	.0239	Total	11.718

$d_p = 0.0239 \pm 0.0017$

EXAMPLE OF CALCULATIONS

The values of D_a' were calculated from equation (6) and by assuming trace conditions and substituting

$$\left[\frac{c_o'}{c_o}\right]^{1/4} = \frac{D_a}{D_a'}$$

into equation (6). K_a values were calculated from equation (11). For example:

2% Nesin and Run number a.

$h = 19.5$ cm $\qquad V_{max.} = 60$ cc

$V_{sat.} = 8$ cc $\qquad V_{max.} - V_{1/2} = 5$ cc

$R = .328$ cc/sec

vfe is calculated from table I.

$$D_a' = \frac{V_{max} - vfe + \left[c_o/c_o\right] V_{sat}/2}{vfe}$$

$$= \frac{5 - 0.1683 \times 19.5 \quad 0.2041 \times 4}{0.1683 \times 19.5}$$

$$= 13.64$$

$$K_a = \frac{4 \ln 2 \, R}{vfe}\left[\frac{V_{max} - vfe + \left[c_o'/c_o\right]^{1/4} V_{sat}/2}{V_{1/2} - V_{max}}\right]^2$$

$$= \frac{(2.77).328}{(19.5)0.1683}\left[\frac{5 - 0.1683(19.5) \; 0.2041(4)}{5}\right]^2$$

$$= 14.5$$

TABLE XVIII

DISTRIBUTION COEFFICIENT FOR 2% RESIN

Run	D_a	$D_a - \bar{D}_a$	$(D_a - \bar{D}_a)^2$
a	13.64	1.207	1.457
b	13.695	1.152	1.327
c	12.145	2.702	7.3008
d	19.207	5.360	28.730
e	14.751	0.096	0.0092
f	9.7500	5.097	25.979
g	17.980	3.133	9.816
h	17.608	2.761	7.623
Mean	14.847		Total 82.242

D_a, distribution constant = 14.847 ± 1.134

TABLE XIX

DISTRIBUTION COEFFICIENT FOR 4% RESIN

Run	D_a	$D_a - \bar{D}_a$	$(D_a - \bar{D}_a)^2$
a	14.454	1.005	1.010
b	11.865	1.584	2.509
c	14.027	0.576	0.332
Mean	13.448	Total	3.851

D_a, distribution constant = 13.448 ± 0.654

d	Void		
e	9.8236	0.3940	0.15524
f	9.4961	0.7215	0.52056
g	11.3306	1.1130	1.2388
Mean	10.2176	Total	1.9146

D_a, distribution constant = 10.2176 ± 0.4612

TABLE XX

DISTRIBUTION COEFFICIENT FOR 8% RESIN

Run	D_a	$D_a - D_a$	$(D_a - D_a)^2$
a	14.198	2.236	5.0000
b	13.426	1.464	2.143
c	15.453	3.491	12.187
d	14.866	2.904	8.433
e	7.148	4.813	23.165
f	9.208	2.753	7.579
g	9.432	2.529	6.396
Mean	11.9262		Total 64.903

D_a, distribution constant = 11.962 ± 1.151

TABLE XXI

DISTRIBUTION COEFFICIENT FOR 16% RESIN

Run	D_a	$D_a - \bar{D}_a$	$(D_a - \bar{D}_a)^2$
a to d	Void		
d	12.305	0.318	0.1011
e	12.919	0.296	0.0876
f	12.509	0.114	0.0130
g	Void		
h	12.305	0.318	0.1011
i	14.425	1.802	3.2472
j	12.529	0.094	0.0088
k	13.034	0.411	0.1689
l	10.760	1.863	3.471
m	12.856	0.233	0.0543
n	Void		0.0008
o	Void		0.0038
p	12.651	0.028	0.0008
q	12.561	0.062	0.0038
Mean	12.623	Total	7.258

D_a, distribution constant = 12.623 ± 0.2449

TABLE XXII

K_a, THE RATE CONSTANT FOR 2% RESIN

Run	K_a	$K_a - K_{a(mean)}$	$(K_a - K_{a(mean)})^2$
a	14.5	7.74	59.91
b	23.0	1.20	1.44
c	20.9	.99	.98
d	33.5	11.65	135.72
e	36.52	14.67	215.21
f	12.53	9.32	86.86
g	17.03	4.82	23.23
h	16.78	5.07	25.70
Mean	21.85		Total 549.05

K_a, rate constant = 21.85 ± 2.92

TABLE XXIII

RATE CONSTANT VALUES FOR 4% RESIN

Run	K_a	$K_a - K_{a(mean)}$	$(K_a - K_{a(mean)})^2$
a	29.9	7.14	50.98
b	19.9	2.86	8.18
c	18.49	4.27	18.23
Mean	22.76		Total 77.39

K_a, rate constant = 22.76 ± 2.93

d	Void		
e	Void		
f	3.42		1.23
g	5.63		1.21
Mean	4.53		Total 2.44

K_a, rate constant = 4.53 ± .781

TABLE XXIV

RATE CONSTANT VALUES FOR 8% RESIN

Run	K_a	$K_a - K_{a(mean)}$	$(K_a - K_{a(mean)})^2$
a	6.87	.86	.74
b	12.33	6.32	39.94
c	7.404	1.39	1.93
d	7.10	1.09	1.19
e	2.68	3.32	11.02
f	2.70	3.31	10.96
g	3.00	3.01	9.06
Mean	6.01		Total 74.84

K_a, rate constant = 6.01 ± 1.24

TABLE XV

RATE CONSTANT VALUES FOR 16% RESIN

Run	K_a	$K_a - K_{a(mean)}$	$(K_a - K_{a(mean)})^2$
d	.73	2.04	4.162
e	2.43	.34	.116
f	2.23	.54	.292
h	3.64	.87	.757
i	3.18	.41	.168
j	2.89	.12	.144
k	3.12	.35	.125
l	2.64	.13	.169
m	5.36	2.59	6.708
p	2.03	.74	.548
q	2.24	.53	.281
Mean	2.77		Total 13.47

K_a, rate constant = $2.77 \pm .33$

DISCUSSION

It can be shown that the equations of Gilliland and Baddour (1953), Boyd et al (1947), and Vermeulen and Heister (1952) are equal using the assumption that the column is under trace conditions. Gilliland and Baddour's (1953) equation shows that their rate constant is equal to Vermeulen's rate equation by the following expression:

$$k = \frac{K_a \, fe}{\rho_b \, Q} \qquad (13)$$

where K_a is the rate constant determined by Vermeulen's equations (equation (11)), fe is the void fraction of the column, ρ_b is the density of the resin, and Q is the capacity of the resin. Boyd et al have an equation which when the first term of the summation is used is equal to the solution which Gilliland and Baddour have derived.

Gilliland and Baddour's solution for D_s, the diffusion constant, was 2.0×10^{-6} and 2.5×10^{-6}. Using the relationship between k and K_a, rate constants, the diffusion rate of the 8% cross-linked resin is about 6.7×10^{-6} which does not agree too closely with theirs. They used Dowex-50, however, the commercial resin which has 8% cross-linkage and sizes of 20-50 mesh. Boyd et al reports D_s values of between 3.7 and 1.2×10^{-6} for another resin, Amberlite IR-1.

The D_a', distribution constant, should be constant in all the runs. It was found to vary between 10 and 14.

These variations could be due to the difference in capacity of the resin between the different cross-linkages.

There seemed to be a breaking upward on the end of the curves of the zones (figures 3 to 12). This it is believed was due to a slight mixing of the V_{sat} and the elution solution. It was observed in a column using a colored solution that if the elution solution was added soon after the level of the V_{sat} had reached the top of the resin that there was considerable mixing.

CONCLUSIONS

Gilliland and Baddour (1953) have an equation for D_s, the diffusion constant. Since we have derived an equation (13) between their k, rate constant, and Vermeulen's K_a, rate constant, by correct evaluation one obtains

$$D_s = \frac{K_a \, d_p^2}{4\pi^2 \, D_a'}$$

where D_s is the diffusion constant, K_a is the rate constant, d_p is the particle diameter, and D_a' is the distribution constant. By substitution of the mean values of K_a, rate constant, and D_a', the distribution constant, one obtains the mean values of D_s (table XXVI). The D_s values have a definite trend therefore an equation can be evaluated.

In order to fit a number of points to a equation the easiest method is by plotting, therefore a plot on ordinary graph paper, semi-log and log paper was made. If a straight line is obtained the curve is a straight line, exponential or power curve. Since the points (table XXVI) seem to give the best straight line on log paper (figure 14) it is assumed that it is a power curve.

The general equation for the power curve is $y = a\,x^n$. By taking the log of both sides we obtain $\log y = \log a + n \log x$ and by substitution of $X = \log x$, $Y = \log y$, $m = n$, and $b = \log a$ we obtain

$$Y = mX + b$$

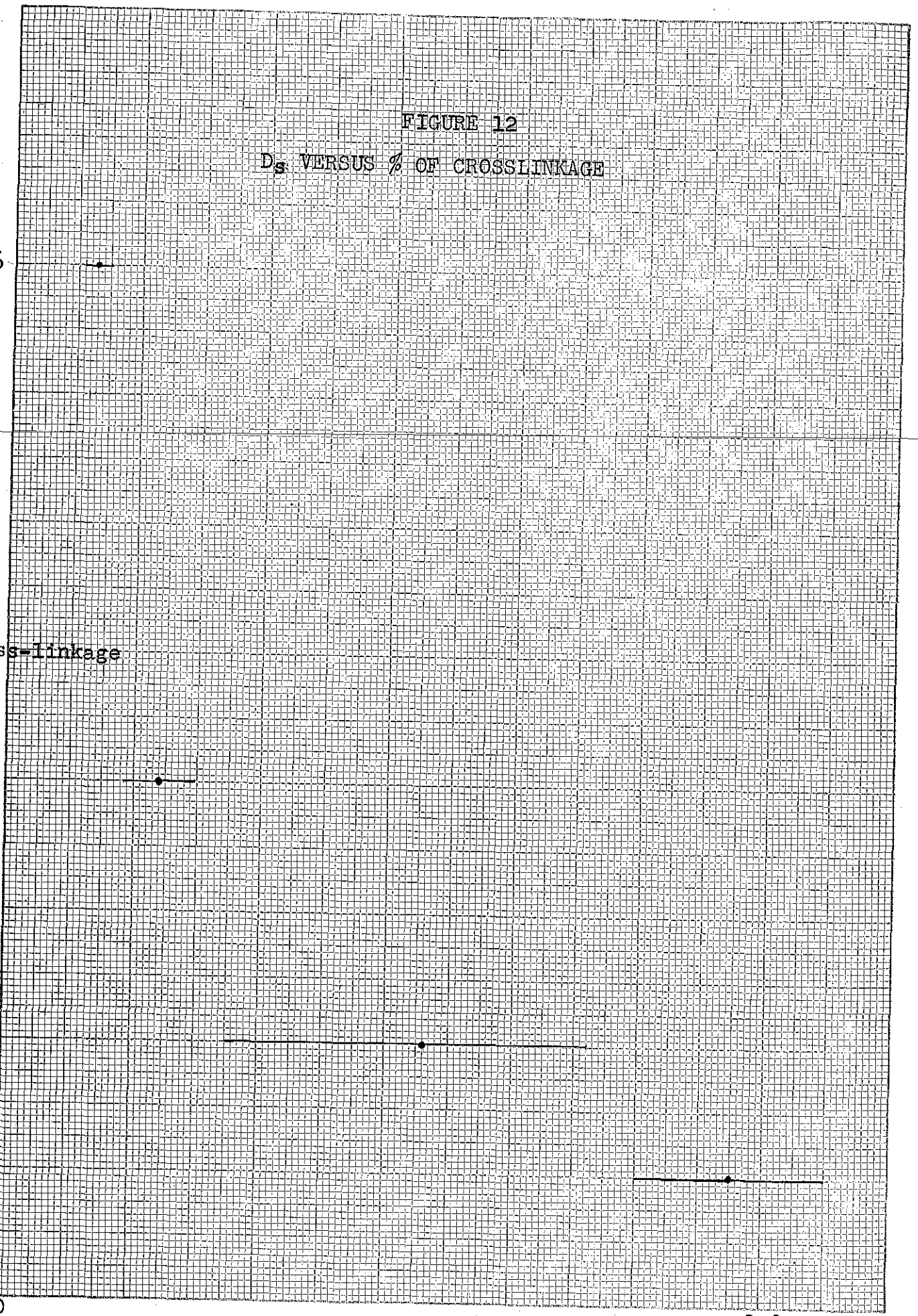
TABLE XXVI

SUMMARY OF D_s VALUES USING $K_{a(mean)}$ AND $D'_{a(mean)}$ VALUES

% Cross-linkage	$D_s \times 10^5$
2 (40-60 Mesh)	2.9 ± 0.43
4 (40-60 Mesh)	1.66 ± 0.76
4 (60-80 Mesh)	3.17 ± 0.44
8 (60-80 Mesh)	0.60 ± 0.13
16 (60-80 Mesh)	0.32 ± 0.05

FIGURE 12

D_s VERSUS % OF CROSSLINKAGE



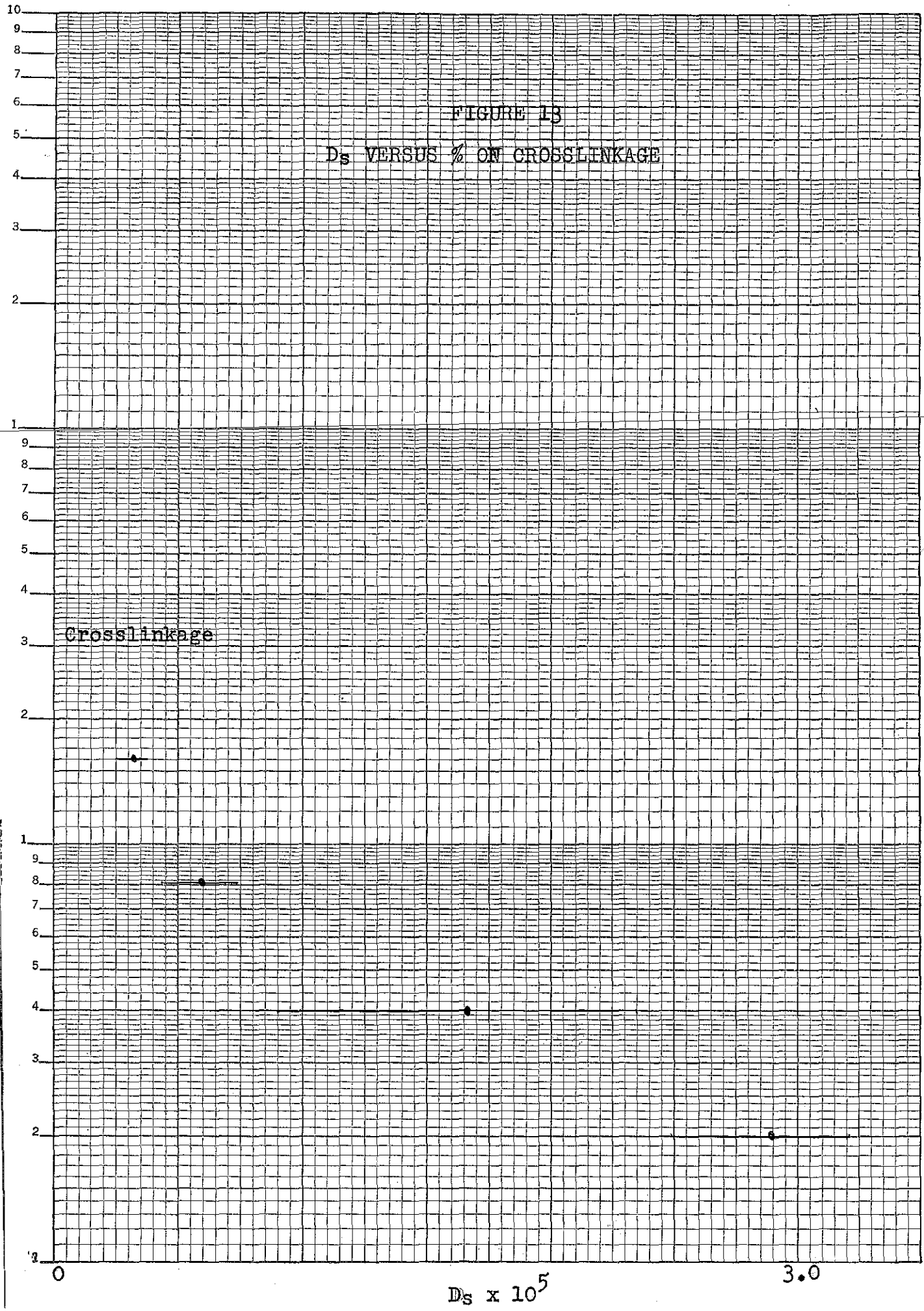
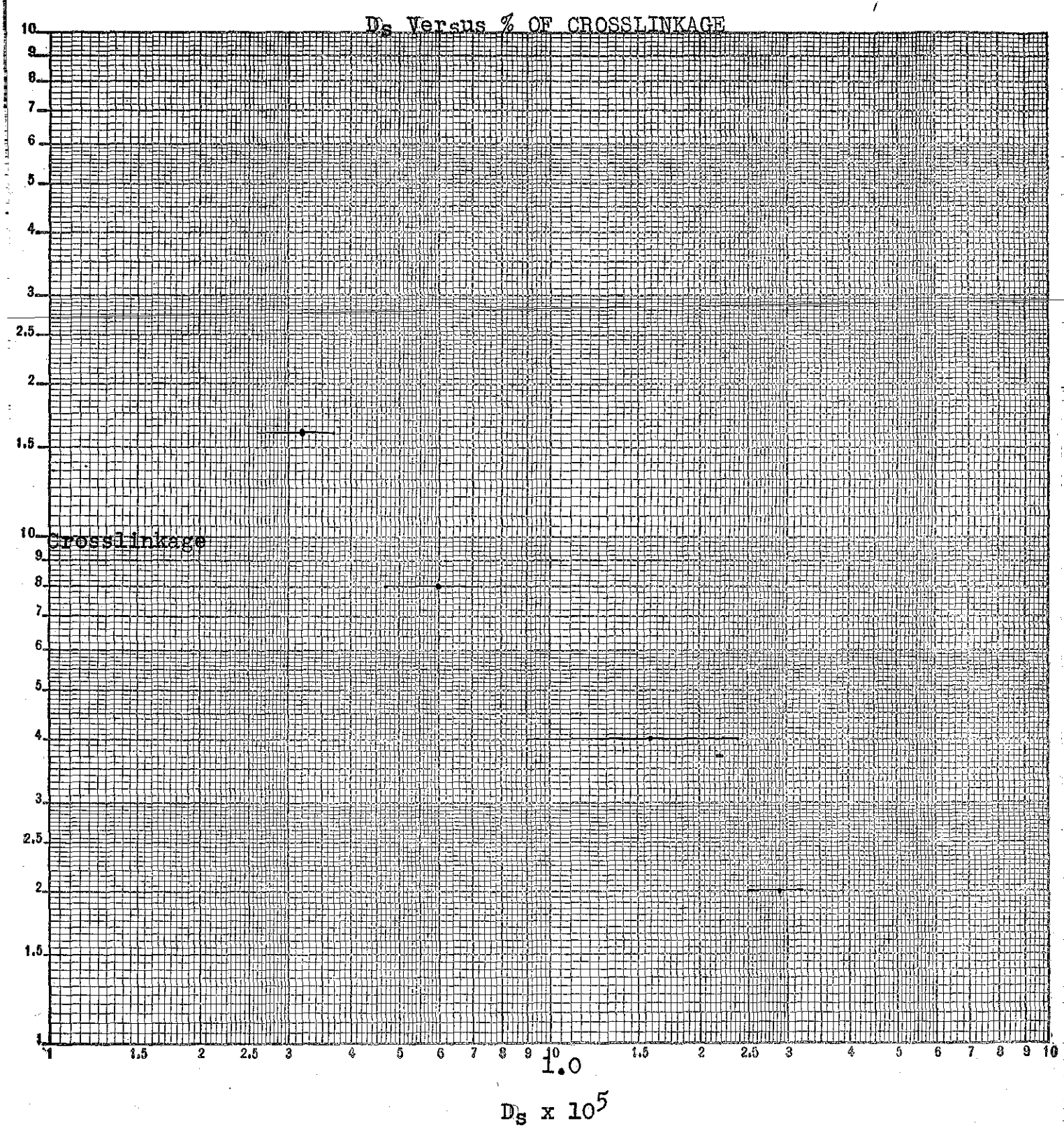


FIGURE 13
D_s VERSUS % OF CROSSLINKAGE
Crosslinkage
10
9
8
7
6
5
4
3
2
1
9
8
7
6
5
4
3
2
1
9
8
7
6
5
4
3
2
1
0
3.0
$D_s \times 10^5$

FIGURE 14


D_s Versus % OF CROSSLINKAGE
Crosslinkage
10
9
8
7
6
5
4
3
2.5
2
1.5
1
1.5
2
2.5
3
4
5
6
7
8
9
10
1.0
$D_s \times 10^5$

By substitution of two of the points on the curve we obtain two simultaneous equations which can be solved.

$$(0.4624)m + b = 0.30103$$

and

$$(1.50515)m + b = 1.20412$$

when $x = D_s \times 10^5 = 2.9$, and 0.32; y = cross-linkage of the resin = 2, and 16 respectively.

Solving for m we obtain

$$m = -0.459 \qquad \times \quad -.866$$

and by substitution

$$b = 1.6631$$

$$b = \log a$$

therefore

$$a = 46.04$$

Therefore the total equation is

$$y = 46.04\, x^{-0.459}$$

where y is the cross-linkage of the resin, and x is the diffusion constant $\times 10^5$.

Note:

Within limits of error, diffusion const is simple inversely proportional to 1st power of cross-linkage.

NOMENCLATURE

Dimensions are given to give an idea of the units. These terms are used throughout the paper. The primes, ', are for the elution values.

a	The trace component of the system
c_o	Total concentration of solutes in fluid phase entering the column; moles per ml.
d_p	Mean diameter of ion exchange particle; cms.
d_w	Inside diameter of the column; cm.
D_a	Distribution ratio or partition coefficient for the trace component A.
D_i	Internal diffusion; square cm. per second.
f_o	Ratio of void space outside particles of adsorbent to total volume of packed column.
G	Ionic carrier component.
h	Height or length of column, cm or ft.
n_a	Total number of moles of component A charged to column during the saturation period.
R	Volumetric flow rate of fluid through fixed solid, ml per second.
s	Column capacity parameter.
S	Cross-sectional area of column, cubic cm. $S = d_w^2/4$
U	Actual linear flow rate of fluid phase through fixed solid, cm per second; Ufo is the superficial linear flow rate through an unpacked column of the same diameter.

u_f linear flow rate of the zone, cm/sec.

v Bulk-packed volume of column cubic cm; $v = h S$; vfe is the void volume of the column.

V Volume of saturating fluid fed to column, cubic cm.

α Valence of trace ion A.

γ Valence of carrier ion G.

ν Kinematic viscosity, square cm. per second.

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